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Concentrations and Sources of VOCs in Urban Domestic and Public Microenvironments

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Concentrations of 15 VOCs including 1,3-butadiene, benzene, and styrene were measured in a wide range of urban microenvironments, viz: homes, offices, restaurants, pubs, department stores, coach and train stations, cinemas, libraries, laboratories, perfume shops, heavily trafficked roadside locations, buses, trains, and automobiles. For most target VOCs—including 1,3-butadiene and benzene—mean concentrations at heavily trafficked roadside locations were exceeded by those in automobiles and were comparable to those in pubs and train stations. With regard to indoor–outdoor relationships in homes, this study revealed higher mean indoor concentrations, no correlation between simultaneously measured indoor and outdoor concentrations, and significantly different patterns of diurnal variation. Thus—in poorly ventilated buildings—indoor emission source strength is considered a more significant influence on VOC concentrations than infiltration of outdoor air. In the six smoking homes studied, environmental tobacco smoke (ETS) was found to make a substantial contribution to concentrations of 1,3-butadiene. This finding was based on the significantly higher concentrations detected in smoking compared to nonsmoking homes, the significant correlation between 1,3-butadiene concentrations and those of 3-ethenylpyridine (an ETS marker), factor analysis, and the results of a source apportionment exercise based on ratios of 1,3-butadiene to 3-ethenylpyridine.

Introduction

Studies of indoor airborne concentrations of volatile organic compounds (VOCs) are urgently required, due to their adverse human health effects, the existence of a large number of indoor emission sources, and the fact that in modern urban areas, people spend more than 70% of their time indoors (*1*). The situation is complicated by the existence of a wide range of indoor microenvironments, such as homes, offices, restaurants, pubs, stores, cinemas, libraries, coach and train stations, etc. Each of these microenvironments are impacted by one or more potential sources of VOCs, including the following: the use of solvents and petroleum related consumer products, building or furnishing materials, heating and cooking equipment such as gas stoves and kerosene or oil heaters, infiltration of outdoor VOCs, and Environmental Tobacco Smoke (ETS) (*1–5*). Most previous studies have focused on a limited range of indoor environments, specifically homes and offices (*6–10*), with the result that few data exist on VOC concentrations in public microenvironments. This is potentially significant, as densely populated public microenvironments such as pubs, restaurants, and coach stations are likely to be strongly influenced by significant VOC sources such as ETS and vehicular emissions.

Previous studies of VOCs in indoor environments have also been restricted with respect to the VOCs monitored. In particular, 1,3-butadiene has been omitted from most previous studies, due to a lack of validated methods for its sampling and analysis at ambient concentrations. Given that it has been identified as a genotoxic carcinogen for which no absolutely safe level of human exposure may be determined (*11*) and that the United States Environmental Protection Agency (USEPA) has classified it as a probable carcinogen with an estimated unit risk factor almost 30 times higher than that of benzene (*12*), this is a potentially serious omission from current assessments of the human health risks arising from indoor air quality.

This study reports the concentrations of 15 VOCs including 1,3-butadiene, benzene and styrene, in a wide range of microenvironments, viz homes, offices, restaurants, pubs, department stores, coach and train stations, cinemas, libraries, laboratories, perfume shops, heavily trafficked roadside locations, buses, trains, and automobiles. Indoor–outdoor concentration ratios for homes are measured via simultaneous indoor:outdoor sampling, and the contribution of ETS to VOC concentrations in six smoking homes (i.e. those inhabited by smokers) is assessed.

Experimental Methodology

Selection of Microenvironments. In modern societies, urban dwellers frequent four principal groups of microenvironments, specifically homes, public microenvironments, transportation microenvironments, and occupational microenvironments. In all, 15 microenvironment categories covering these four groups were selected. All were located within a 3 km radius of central Birmingham, with full details given in Table 1. Public microenvironments selected consisted of department stores, libraries, restaurants, pubs, coach and train stations, cinemas, and perfume shops, while the transportation microenvironments chosen were heavily trafficked roadside locations and the interiors of buses, trains, and automobiles.

To facilitate evaluation of the contribution of ETS to VOC concentrations, six smoking and six nonsmoking homes were selected. Smoking homes were defined as those in which at least one smoker was residing, and in which smoking occurred during sampling. In all bar one home, electricity was used for cooking and gas heaters were not used during sampling. Three homes were located within 10 m of a heavily trafficked road. The diurnal variation of VOC concentrations was measured in one smoking and one nonsmoking home. In the remaining 10 homes, sampling was conducted between the following periods: 12:00 to 14:00, 18:00 to 22:00, and 24:00 to 02:00, representing concentrations during the day, evening, and night, respectively.

Sampling and Analytical Methods. Analyte Selection Criteria. VOCs monitored in this study were selected according to the following criteria: (a) adverse human health effects, in particular carcinogenicity (1,3-butadiene, benzene, and styrene), (b) the extent of previous monitoring, and (c) potential utility as a tracer of a specific emission source—e.g. 3-ethenylpyridine for ETS.

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TABLE 1. Description of Microenvironments Monitored

microenvironment	location	sampling conditions	smoking status	N[a]
homes (12[b])	around University of Birmingham	3 times per home per day simultaneous sampling indoors and outdoors (12:00–14:00; 18:00–22:00; 24:00–02:00)	yes (6 homes) no (6 homes)	128
offices (6)	in University of Birmingham	twice per office per day (09:30–11:30; 14:00–16:00)	no	12
laboratories (4)	in University of Birmingham	twice per laboratory per day (09:30–11:30; 14:00–16:00)	no	8
cinemas (2)	in City center	3 times per cinema (during movie time)	no	6
department stores (2)	in City center	twice per department store per day on 2 days (09:30–11:30; 14:00–16:00)	no	8
perfume shops (3)	in City center (2 places)	once per shop	no	3
libraries (3)	in University of Birmingham	twice per library per day (09:30–11:30; 14:00–16:00)	no	6
pubs (6)	around University of Birmingham (3 pubs); in City center (3 pubs)	once per pub	yes	6
restaurants (6)	in City center	once per restaurant	yes	6
train stations (2)	in City center	3 times per train station per day on 2 days sampling at waiting area and platform (07:30–09:30; 12:00–14:00; 17:00–19:00)	no	12
coach stations (1)	in City center	6 times per coach station per day on 2 days sampling at waiting area and platform (07:30–09:30; 12:00–14:00; 17:00–19:00)	no (in waiting area); yes (on coach platform)	12
trafficked roadside locations (4)	in City center (1 road); around University of Birmingham (3 roads)	3 times per road (07:30–09:30; 12:00–14:00; 17:00–19:00)	no	12
automobiles (12)	cars driven inside Birmingham city	3 times per automobile per day (08:00–09:00; 12:00–13:00; 18:00–19:00)	yes (6 cars) no (6 cars)	36
buses (18)	bus services inside Birmingham city	once per bus per day	no	18
trains (18)	train services inside Birmingham city	once per train per day	no	18

[a] *N* is the number of samples collected in the microenvironment. [b] The number of places selected.

TABLE 2. TD/GC/MS Operating Conditions for VOCs Other Than 1,3-Butadiene

TD (Tekmar 6000)		GC (HP 5890 series II)		MSD (HP 5971A)	
parameter	value	parameter	value	parameter	value
desorb temp.	250 °C	initial temp.	40 °C	interface temp.	250 °C
desorb time	20 min	final temp.	180 °C	EMV[a]	2494
valve temp.	200 °C	initial time	5 min	mode	SIM
trap high	375 °C	final time	1 min	tune masses	69, 131, 219
trap low	−30 °C	oven ramp rate	5 °C/min	interface type	capillary D.[b]
trap hold	5 min	carrier pressure	14.5 psi		
line temp.	200 °C	carrier gas	helium		

[a] Electron multiplier voltage. [b] Capillary direct.

Since 1,3-butadiene differs considerably from the other VOCs monitored with respect to adsorption/desorption characteristics and susceptibility to decomposition/artifact formation, it was monitored using a different protocol to that employed for the other 14 targeted VOCs (benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, styrene, *p*-isopropyltoluene, 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, naphthalene, pyridine, and 3-ethenylpyridine).

Sampling Method. Sampling was conducted between November 1999 and February 2000 using adsorbent tubes fitted to a personal pump operated at a flow rate of ca. 40 mL min^{-1}. For 1,3-butadiene, the adsorbent tube was packed with 1000 mg of Carbopack B (60/80 mesh, Supelco) followed by 150 mg of Carbosieve SIII (60/80 mesh, Supelco) (*13*), while the other VOCs were trapped on an adsorbent tube packed with 300 mg of Tenax GR (60/80 mesh, Chrompack) followed by 600 mg of Carbotrap (20/40 mesh, Supelco). The duration of sampling time varied according to the microenvironment, with details given in Table 1. Each adsorbent tube was capped with swagelok fittings before and after sampling.

Analytical Method. Analysis of all VOCs was conducted using a thermal desorber (Tekmar 6000/6016) interfaced with a gas chromatograph (HP 5890 series II) and mass selective detector (HP 5971A). Chromatographic separation was achieved using a PLOT capillary column (50 m, 0.32 mm i.d., 5 μm film thickness, Chrompack) for 1,3-butadiene and a Stabil-wax capillary column (50 m, 0.25 mm i.d., Restek) for the other VOCs. The analytical conditions for 1,3-butadiene are described elsewhere (*13*), but those for the other VOCs are given in Table 2. For 1,3-butadiene, calibration was achieved via introduction of an appropriate aliquot of 1,3-butadiene standard gas (10 ppm, BOC speciality gases) onto an adsorbent tube, via a gas valve and sample loop. For other VOCs, calibration was conducted using a standard liquid mixture spiked onto an adsorbent tube. In each case, calibration standards were analyzed before and after analysis of each batch of samples. Note that in this study, 4-ethenylpyridine was used for the calibration of 3-ethenylpyridine. This was considered justified, given that reference standards of 3-ethenylpyridine were not commercially available during this work, and because the mass fragmentation patterns of the two isomers are similar (*14*).

Method Validation. Extensive validation was conducted of our sampling and analytical methodology. A detailed description of our method validation techniques for VOC analysis as applied to 1,3-butadiene is given elsewhere (*13*).

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As the same techniques were applied to the validation of our methods for the other target VOCs, only the results of our validation studies will be discussed here.

Field Blanks. Ten field blanks (i.e. clean sealed sorbent tubes stored next to a sampler during a sampling event prior to analysis) were tested with no significant contamination found for any of the target VOCs.

Storage Stability. Although our sampling protocol permits a maximum delay between sampling and analysis of 48 h, with storage at −18 °C wherever possible, storage stability was evaluated for all target VOCs. When stored at ambient temperature, 1,3-butadiene was stable for at least 2 days, and at least 7 days when stored at −18 °C. All other VOCs including benzene were stable for at least 2 weeks at ambient temperatures.

Breakthrough. For 1,3-butadiene, this was evaluated at a concentration of 27.9 $\mu g\ m^{-3}$, compared to the maximum concentration recorded in this study of 20.1 $\mu g\ m^{-3}$. For other VOCs, breakthrough was evaluated for benzene and toluene which—respectively—are the most volatile and abundant of the VOCs monitored. Breakthrough was evaluated at concentrations of 830 and 1480 $\mu g\ m^{-3}$ for benzene and toluene, respectively. By comparison, the highest concentrations recorded in this study were 720 and 1300 $\mu g\ m^{-3}$, respectively. No breakthrough was observed for any VOCs in our tests, and it is not considered to influence our data.

Linearity, Precision, and Detection Limits. Linearity of detector response for all VOCs was evaluated using five point calibrations covering the full range of concentrations recorded in this study. The correlation coefficient for all calibration plots exceeded 0.996 ($p \leq 0.05$). Analytical precision was found to be less than 7.6% for all target VOCs. In addition, the precision of sampling and analysis *combined* was evaluated by acquiring six spatially and temporally consistent samples. Subsequent analysis revealed precision to be better than 10% for all target VOCs except 1,3,5-trimethylbenzene (11.5%), *p*-isopropyltoluene (11.7%), and pyridine (14.5%). Method detection limits (MDLs) were calculated according to the method of Glazer et al. (*15*) and found to be <0.32 $\mu g\ m^{-3}$ for all compounds, with those for 1,3-butadiene, benzene, and styrene determined to be 0.11, 0.26, and 0.21 $\mu g\ m^{-3}$, respectively. In this study, concentrations of *p*-isopropyltoluene and 1,4-dichlorobenzene were below the MDL in 32% and 58% of samples, respectively. Therefore, although concentrations of these compounds are reported as an addition to the scientific database, they are excluded from the ensuing discussion.

Results and Discussion

Concentrations of VOCs in Microenvironments. Concentrations of individual VOCs varied widely according to the microenvironment. Mean concentrations ($\mu g\ m^{-3}$) and standard deviations for each VOC in each microenvironment are shown in Table 3. Mean concentrations of most VOCs were elevated in transportation microenvironments such as automobiles, roadside locations, buses, and trains. Of the public microenvironments monitored, pubs and train stations were shown to have the highest concentrations of most target VOCs. Given the presence of well characterized VOC emission sources such as vehicles and ETS in such microenvironments, the higher concentrations recorded are not unexpected.

In all transportation microenvironments, the highest mean concentrations of 1,3-butadiene and benzene of 7.9 $\mu g\ m^{-3}$ and 203.7 $\mu g\ m^{-3}$, respectively, were detected in automobiles. Cars were also shown to have the highest mean concentrations of all other target VOCs, except for pyridine, 3-ethenylpyridine, 1,4-dichlorobenzene, and *p*-isopropyltoluene. However, all 12 automobiles used in this study were over 10 years old. Furthermore, smoking occurred in six

TABLE 3. Mean Concentrations ($\mu g\ m^{-3}$) of VOCs in Different Microenvironments[a]

VOC	homes (64)[a]	offices (12)	rest. (6)	pubs (6)	dep. st. (8)	cinemas (6)	p.i. shop (3)	libraries (6)	labs (8)	t. sta. (12)	c. sta. (12)	t. roads (12)	cars (35)	trains (18)	buses (18)
1,3-butadiene	1.1[b] (1.9)[c]	0.3 (0.2)	1.5 (0.8)	3.0 (2.0)	0.6 (0.4)	0.6 (0.3)	0.9 (0.1)	0.4 (0.2)	0.2 (0.1)	2.2 (1.7)	0.9 (0.7)	1.8 (0.9)	7.9 (4.7)	1.0 (0.6)	1.7 (0.9)
benzene	13.9 (13.8)	5.9 (2.3)	22.7 (4.0)	31.7 (33.5)	10.5 (5.6)	15.5 (9.1)	6.8 (1.2)	8.8 (2.5)	4.2 (1.6)	46.5 (37.7)	20.0 (16.1)	49.6 (22.4)	203.7 (152.3)	24.3 (35.8)	20.2 (7.8)
toluene	38.4 (21.7)	22.0 (14.4)	57.0 (20.2)	75.4 (79.7)	56.7 (29.2)	43.6 (28.3)	43.8 (26.7)	21.2 (9.7)	8.3 (3.1)	135.3 (117.1)	47.3 (33.8)	108.1 (50.3)	494.0 (283.6)	64.9 (119.7)	69.3 (30.9)
ethylbenzene	2.3 (1.3)	2.4 (1.3)	6.2 (3.0)	7.3 (11.4)	3.4 (2.4)	5.9 (5.6)	2.4 (0.1)	3.5 (2.8)	0.7 (0.2)	7.4 (7.6)	3.8 (1.3)	12.4 (8.6)	51.9 (30.8)	5.6 (8.8)	8.0 (3.9)
p-xylene	1.9 (1.1)	1.7 (0.7)	5.6 (2.8)	6.5 (10.4)	3.1 (2.2)	5.5 (5.3)	2.2 (0.1)	3.1 (2.7)	0.6 (0.2)	6.9 (7.5)	3.5 (1.0)	11.6 (8.4)	52.5 (31.5)	4.8 (8.5)	7.8 (3.9)
m-xylene	5.3 (3.2)	6.0 (3.6)	16.3 (8.2)	18.3 (28.6)	8.9 (6.4)	15.7 (14.1)	6.0 (0.3)	9.2 (8.2)	1.9 (0.9)	18.8 (18.7)	10.1 (3.7)	32.3 (21.2)	127.2 (76.8)	13.2 (20.4)	20.3 (10.2)
o-xylene	1.9 (1.3)	1.8 (0.6)	6.0 (2.9)	6.9 (11.2)	3.5 (2.5)	5.9 (5.3)	2.4 (0.3)	3.3 (2.7)	0.8 (0.3)	7.5 (8.1)	3.5 (1.3)	13.2 (9.7)	54.2 (33.6)	5.0 (8.3)	8.6 (4.1)
1,3,5-TMB	0.5 (0.5)	0.3 (0.1)	1.3 (0.7)	1.5 (2.3)	0.8 (0.5)	1.7 (1.3)	0.5 (0.1)	1.1 (0.9)	0.1 (0.0)	1.5 (1.5)	0.8 (0.3)	2.8 (3.0)	9.4 (5.9)	1.0 (1.6)	2.3 (1.1)
styrene	0.8 (0.7)	0.6 (0.5)	1.4 (1.1)	2.1 (2.2)	1.1 (0.5)	0.7 (0.6)	0.7 (0.5)	0.5 (0.4)	0.2 (0.1)	1.4 (0.9)	0.6 (0.4)	1.7 (1.5)	4.3 (3.1)	1.4 (1.4)	0.7 (0.3)
p-IPT	0.9 (1.2)	0.3 (0.2)	0.6 (0.3)	0.8 (0.7)	0.5 (0.1)	4.9 (10.5)	2.0 (0.8)	0.3 (0.2)	0.2 (0.3)	0.2 (0.1)	0.4 (0.6)	0.2 (0.3)	1.0 (1.9)	0.4 (0.4)	0.6 (0.3)
1,2,4-TMB	1.7 (1.9)	1.5 (0.5)	5.9 (3.5)	6.2 (10.0)	3.4 (2.2)	7.6 (5.4)	2.9 (0.3)	4.8 (3.2)	0.5 (0.2)	6.3 (5.5)	3.8 (1.9)	10.9 (10.5)	33.9 (21.5)	4.1 (5.4)	11.8 (5.4)
1,4-DCB	0.1 (0.2)	0.1 (0.1)	2.9 (6.5)	2.3 (4.4)	23.4 (35.4)	0.3 (0.3)	1.7 (0.7)	12.8 (27.7)	0.1 (0.0)	0.2 (0.1)	0.7 (0.7)	0.1 (0.1)	1.3 (5.5)	0.4 (0.4)	2.4 (2.0)
3-ethenylpyridine	0.4 (1.1)	nd[e] (–)	0.6 (1.0)	3.8 (4.4)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	0.1 (0.4)	nd[e] (–)	1.9 (3.9)	nd[e] (–)	nd[e] (–)
naphthalene	0.8 (1.0)	1.7 (3.2)	0.9 (0.4)	1.0 (1.0)	0.7 (0.4)	0.6 (0.3)	0.4 (0.2)	0.5 (0.3)	0.1 (0.0)	1.6 (0.9)	1.1 (1.9)	12.1 (38.0)	5.0 (3.3)	1.0 (0.9)	0.9 (0.3)
pyridine	0.4 (1.2)	nd[e] (–)	0.6 (0.9)	3.3 (3.8)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	nd[e] (–)	0.1 (0.2)	nd[e] (–)	1.7 (3.5)	nd[e] (–)	nd[e] (–)

[a] Number of samples collected. [b] Mean concentration. [c] Standard deviation. [d] rest. (restaurant), dep. st. (department store), p.f. shop (perfume shop), t. sta. (train station), c. sta. (coach station), t. roads (trafficked roads); 1,3,5-TMB (1,3,5-trimethylbenzene), *p*-IPT (*p*-isopropyltoluene), 1,2,4-TMB (1,2,4-trimethylbenzene), 1,4-DCB (1,4-dichlorobenzene). [e] nd = not detected.

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TABLE 4. Comparison of Indoor and Outdoor VOC Concentrations ($\mu g\ m^{-3}$) for 12 Homes[d]

VOC	indoor ($n = 64$) mean	SD	median	min	max	outdoor ($n = 64$) mean	SD	median	min	max	I/O[a] ratio	Wilcoxon test[b]
1,3-butadiene	1.1	1.9	0.5	nd[e]	10.8	0.3	0.2	0.3	nd[e]	0.9	6.6	+[c]
benzene	13.9	13.8	9.2	3.4	63.7	7.3	6.0	5.1	0.7	29.8	3.4	+[c]
toluene	38.4	21.7	34.8	8.8	99.3	15.1	12.7	11.2	2.2	75.7	4.0	+[c]
ethylbenzene	2.3	1.3	2.0	0.6	6.5	1.6	1.4	1.2	0.2	8.4	2.3	+[c]
p-xylene	1.9	1.1	1.6	0.5	5.4	1.4	1.3	1.1	0.2	7.3	2.2	+[c]
m-xylene	5.3	3.2	4.5	1.3	16.1	3.8	3.7	3.0	0.5	22.5	2.3	+[c]
o-xylene	1.9	1.3	1.6	0.4	6.3	1.4	1.3	1.2	0.2	7.6	2.1	+[c]
1,3,5-TMB	0.5	0.5	0.3	nd[e]	2.3	0.3	0.2	0.2	nd[e]	1.2	2.1	+[c]
styrene	0.8	0.7	0.5	nd[e]	3.4	0.4	0.7	0.2	nd[e]	4.4	4.3	+[c]
1,2,4-TMB	1.7	1.9	1.0	0.3	8.6	1.1	0.9	0.8	nd[e]	5.2	2.1	+[c]
3-ethenylpyridine	0.4	1.1	nd[e]	nd[e]	5.9	-	-	nd[e]	nd[e]	nd[e]	-	+[c]
naphthalene	0.8	1.0	0.5	0.2	6.0	0.3	0.2	0.2	nd[e]	0.9	4.2	+[c]
pyridine	0.4	1.2	nd[e]	nd[e]	6.6	-	-	nd[e]	nd[e]	nd[e]	-	+[c]

[a] The mean of I/O ratios. [b] Wilcoxon test (Wilcoxon rank sum W test). [c] (+) significantly different at the 0.05 level. [d] 1,3,5-TMB (1,3,5-trimethylbenzene), *p*-IPT (*p*-isopropyltoluene), 1,2,4-TMB (1,2,4-trimethylbenzene), 1,4-DCB (1,4-dichlorobenzene). [e] nd = not detected.

automobiles during sampling. It is highly probable that concentrations in newer cars in the absence of smoking would be lower than the mean values recorded in our study, and it is stressed that our limited dataset should not be taken as representative of VOC concentrations in vehicles in general, since the mean age of automobiles monitored in this study (which were all owned by graduate students) is likely to be appreciably greater than that of the U.K. fleet overall.

High VOC concentrations were also found in pubs. In this study, six pubs were selected, with smoking occurring during every sampling event. Mean concentrations of 1,3-butadiene and styrene in pubs were—with the exception of those recorded in cars—the highest recorded at 3.0 $\mu g\ m^{-3}$ and 2.1 $\mu g\ m^{-3}$, respectively.

In this study, mean concentrations of some VOCs in automobiles, pubs, and train stations exceeded or were comparable to those at heavily trafficked roadside locations, which have long been considered as representative worst-case scenarios for air pollution. The presence of elevated concentrations in such widely frequented microenvironments could therefore have appreciable implications for public health.

Indoor Air Quality in Homes. Indoor:Outdoor Concentration Ratios. Mean indoor:outdoor (I/O) concentration ratios of VOCs in homes are given in Table 4. Mean concentrations were higher in indoor air than in outdoor air for all VOCs, as previously reported (*10, 16, 17*). Mean concentrations of 1,3-butadiene and benzene indoors were 1.1 and 13.9 $\mu g\ m^{-3}$, with mean I/O ratios of 6.6 and 3.4, respectively. Interestingly, our data show that indoor concentrations do not always exceed those outdoors, as the maximum concentrations of the xylenes and ethylbenzene recorded outside exceed the maxima recorded indoors. Closer inspection of our data revealed that the maximum outdoor concentrations were recorded outside a home that was located within 10 m of a busy road. The existence of a possible relationship between VOC concentrations recorded indoors and outdoors was statistically evaluated using the Wilcoxon rank sum W test, with results shown in Table 4. This test evaluates whether there are significant differences between two datasets—in this instance indoor and outdoor VOC concentrations. The test is appropriate in this context, as it is a nonparametric test designed for the evaluation of datasets such as these that do not display normal distribution. For all VOCs, indoor and outdoor concentrations were shown to be significantly different ($p \leq 0.05$). The diurnal variations in concentrations of 1,3-butadiene, styrene, benzene, and toluene both indoors and outdoors in one smoking home and one nonsmoking home over a period of 24 h are shown in Figures 1 and 2, respectively. In the nonsmoking home, though the patterns of VOC concentrations are very similar indoors and outdoors, the peak times of these concentrations are not coincident in the two environments. In addition, there is generally a time lag, with the outdoor increase preceding that observed indoors. Furthermore, the rise in indoor concentrations generally starts from a higher baseline than outdoors. In the smoking home, the diurnal variations of VOC concentrations indoors and outdoors are very different with a particularly marked dichotomy observed during smoking events.

The concentration of indoor pollutants is controlled by several factors; the most prominent being the following: the volume of air contained in the indoor environment; the emission/removal rate of the pollutant in the indoor microenvironment; the building ventilation rate; and outdoor concentrations (*18*). In this study, building ventilation rates were not measured but are considered likely to be low, since all sampling was conducted over a period when the average daily *maximum* outdoor air temperature recorded on the University of Birmingham campus was 8.2 °C. Therefore, although it is recognized that the situation may differ in summer or in locations benefiting from a warmer climate—the presence or absence of indoor sources of VOCs is deemed the most important factor controlling the indoor air quality of homes *in this comparatively small study*. This survey revealed higher mean indoor concentrations, no relationship between simultaneously measured indoor and outdoor concentrations, and significantly different patterns of diurnal variation in VOC concentrations recorded indoors and outdoors. Thus—*in poorly ventilated buildings*—indoor emission source strength appears to be a more significant influence on concentrations of VOCs in indoor air than outdoor air concentrations.

VOC Concentrations in Smoking Homes Compared with Nonsmoking Homes. The airborne concentrations of VOCs in six smoking homes and six nonsmoking homes are compared in Table 5. Mean concentrations of 1,3-butadiene and benzene in smoking homes were 1.7 and 16.3 $\mu g\ m^{-3}$ respectively, i.e. 3.4 times and 1.4 times higher than those in nonsmoking homes. Statistical evaluation using the Wilcoxon rank sum W test revealed significant differences between concentrations in smoking and nonsmoking homes for all VOCs except styrene, 1,4-dichlorobenzene, and naphthalene. Interestingly, while concentrations of 1,3-butadiene and benzene were significantly higher in smoking homes, those of most other aromatic VOCs were higher in *nonsmoking* homes. This is a clear indication of the plethora of additional, non-ETS sources of VOCs in domestic mi-

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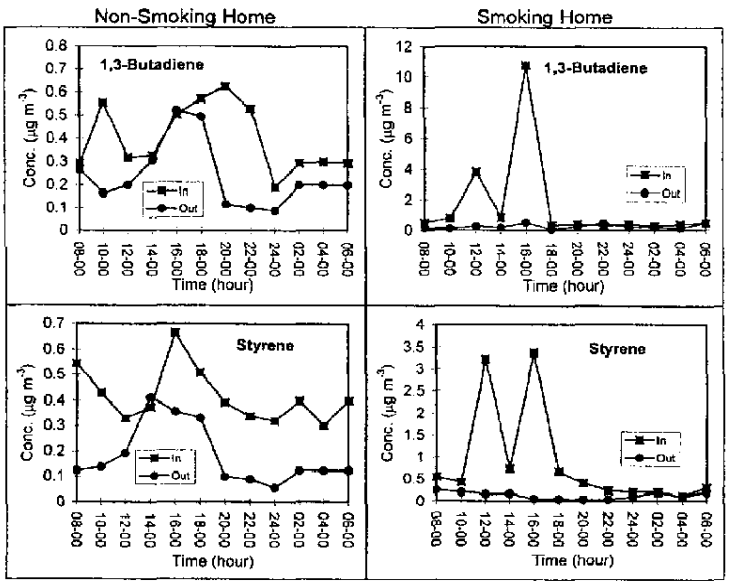

FIGURE 1. The diurnal variation of 1,3-butadiene and styrene in a smoking and nonsmoking home.

TABLE 5. Comparison of VOC Concentrations ($\mu g\ m^{-3}$) in Six Smoking and Six Nonsmoking Homes[a]

	smoking homes ($N = 32$)					nonsmoking homes ($N = 32$)						
VOC	mean	SD	median	min	max	mean	SD	median	min	max	S/NS ratios	Wilcoxon test[a]
1,3-butadiene	1.7	2.5	0.7	0.3	10.8	0.5	0.3	0.4	0.1	1.1	3.4	+[b]
benzene	16.3	15.3	11.4	4.2	63.7	11.5	11.8	6.6	3.4	51.7	1.4	+[b]
toluene	29.2	17.4	28.4	9.6	78.2	47.6	22.0	45.5	8.8	99.3	0.6	+[b]
ethylbenzene	1.9	1.2	1.5	0.6	5.9	2.7	1.2	2.4	1.1	6.5	0.7	+[b]
p-xylene	1.4	0.9	1.2	0.5	5.4	2.4	1.0	2.1	1.0	5.4	0.6	+[b]
m-xylene	4.3	2.9	3.5	1.3	16.1	6.3	3.1	5.5	2.4	15.5	0.7	+[b]
o-xylene	1.4	1.1	1.2	0.4	6.3	2.5	1.3	2.2	1.0	6.0	0.6	+[b]
1,3,5-TMB	0.3	0.4	0.2	0.1	1.4	0.6	0.6	0.4	0.2	2.3	0.5	+[b]
styrene	0.8	0.8	0.5	0.2	3.4	0.7	0.7	0.4	0.3	3.2	1.1	-[c]
1,2,4-TMB	1.2	1.4	0.6	0.3	5.1	2.2	2.1	1.4	0.6	8.6	0.5	+[b]
3-ethenylpyridine	0.8	1.4	0.3	nd[e]	5.9	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]	*f*	+[b]
naphthalene	0.5	0.3	0.5	0.2	1.4	1.0	1.3	0.5	0.2	6.0	0.5	-
pyridine	0.9	1.6	0.1	nd[e]	6.6	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]	*f*	+[b]

[a] Wilcoxon Test (Wilcoxon rank sum W test). [b] (+) significantly different at the 0.05 level. [c] (−) not significantly different at the 0.05 level. [d] 1,3,5-TMB (1,3,5-trimethylbenzene), *p*-IPT (*p*-isopropyltoluene), 1,2,4-TMB (1,2,4-trimethylbenzenel, 1,4-DCB (1,4-dichlorobenzene). [e] nd = not detected. [f] Not calculable.

croenvironments. Examples include the following: infiltration of vehicle exhaust emissions, cooking, and use of solvent-based products. While indoor VOC concentrations in those homes sited within 10 m of a heavily trafficked road displayed no significant elevation compared to other homes, elevated concentrations of inter alia benzene and toluene were recorded in samples taken in a nonsmoking home after cooking fat was overheated. Furthermore, in two of the homes—both also nonsmoking—markedly higher concentrations of many target VOCs were recorded after solvent-based cleaning products and paints were used. Table 6 compares concentrations of selected VOCs before and after cleaning and painting in these homes. These activities provide a likely explanation for the higher mean concentrations of the alkylated monoaromatic hydrocarbons observed in nonsmoking homes in our study. Furthermore, such sources could exert an appreciable influence—additional to that of ETS—on VOC concentrations in smoking homes. It is thus important to note that ETS is just one of many possible sources of these VOCs in smoking microenvironments.

TABLE 6. Concentrations ($\mu g\ m^{-3}$) of Selected VOCs Recorded in Two NonSmoking Homes before and after Use of Solvent-Based Cleaning and Painting Products

VOC	before cleaning	after cleaning	before painting	after painting
1,3-butadiene	0.1	0.4	0.4	1.1
benzene	3.5	12.6	6.1	9.2
toluene	8.8	45.8	21.2	71.2
ethylbenzene	1.2	4.2	3.2	2.5
p-xylene	1.0	3.7	2.7	3.5
m-xylene	3.0	11.2	9.1	6.0
o-xylene	1.0	4.1	2.7	2.3
1,3,5-trimethylbenzene	0.2	0.7	0.4	0.5
styrene	0.3	1.0	0.6	0.5
1,2,4-trimethylbenzene	0.6	2.8	1.6	1.6
naphthalene	0.2	0.7	0.3	0.5

In this study, statistical comparison of 1,3-butadiene and benzene concentrations recorded in both smoking and

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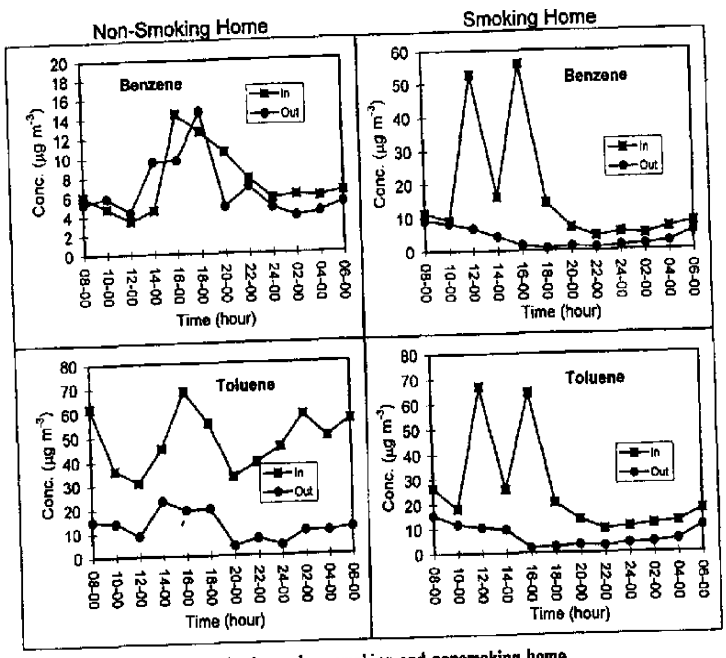

FIGURE 2. The diurnal variation of benzene and toluene in a smoking and nonsmoking home.

TABLE 7. Correlation Coefficients between VOC Concentrations in 12 Homes[a]

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1,3-butadiene	1	1.00														
benzene	2	0.69[b]	1.00													
toluene	3	0.24	0.57[b]	1.00												
ethyl benzene	4	0.29[b]	0.68[b]	0.78[b]	1.00											
p-xylene	5	0.07	0.49[b]	0.80[b]	0.95[b]	1.00										
m-xylene	6	0.20	0.61[b]	0.74[b]	0.98[b]	0.96[b]	1.00									
o-xylene	7	−0.01	0.46[b]	0.74[b]	0.92[b]	0.97[b]	0.96[b]	1.00								
1,3,5-TMB	8	−0.09	0.49[b]	0.55[b]	0.64[b]	0.66[b]	0.67[b]	0.74[b]	1.00							
styrene	9	0.65[b]	0.87[b]	0.51[b]	0.62[b]	0.44[b]	0.56[b]	0.41[b]	0.51[b]	1.00						
p-IPT	10	−0.12	0.08	0.31[b]	0.12	0.19	0.13	0.20	0.52[b]	0.18	1.00					
1,2,4-TMB	11	−0.08	0.51[b]	0.57[b]	0.66[b]	0.68[b]	0.69[b]	0.75[b]	0.99[b]	0.52[b]	0.53[b]	1.00				
1,4-DCB	12	−0.06	0.39[b]	0.31[b]	0.32[b]	0.32[b]	0.35[b]	0.40[b]	0.86[b]	0.44[b]	0.68[b]	0.86[b]	1.00			
3-EP	13	0.86[b]	0.67[b]	0.20	0.30[b]	0.08	0.21	0.00	−0.12	0.68[b]	−0.19	−0.10	−0.13	1.00		
naphthalene	14	−0.03	0.52[b]	0.54[b]	0.52[b]	0.51[b]	0.52[b]	0.55[b]	0.83[b]	0.47[b]	0.27[b]	0.83[b]	0.66[b]	−0.07	1.00	
pyridine	15	0.92[b]	0.72[b]	0.22	0.31[b]	0.07	0.21	−0.02	−0.13	0.69[b]	−0.17	−0.11	−0.12	0.97[b]	−0.08	1.00

[a] 1,3,5-TMB (1,3,5-trimethylbenzene), *p*-IPT (*p*-isopropyltoluene), 1,2,4-TMB (1,2,4-trimethylbenzene), 1,4-DCB (1,4-dichlorobenzene), 3-EP (3-ethenylpyridine). [b] Significant at $p \leq 0.05$.

nonsmoking homes revealed them to be significantly higher ($p \leq 0.05$) in smoking homes than in nonsmoking homes. However, this alone is insufficient evidence to demonstrate that ETS is the source of these elevated concentrations. We therefore evaluated the contribution of ETS to concentrations of all VOCs using 3-ethenylpyridine—a previously proven ETS marker (*8, 14, 19*)—via a combination of correlation and factor analysis. Table 7 shows the correlation coefficients between concentrations of individual VOCs in homes. Concentrations of 1,3-butadiene, benzene, and styrene were significantly correlated ($p \leq 0.05$) with those of 3-ethenylpyridine. The strong correlation between 1,3-butadiene and the ETS marker is confirmed by factor analysis—see Table 8, which shows 1,3-butadiene grouped with 3-ethenylpyridine, benzene, styrene, and pyridine as factor 2. Factor analysis incorporating Varimax rotation was performed on concentrations of all VOCs recorded in all samples collected in smoking homes using SPSS for Windows Version 10.0. Although a number of factors were extracted from the data, only the first three are cited and used for source apportionment, as combined they accounted for 88% of the total variance of the original sample set, and no additional relevant information was provided by the other three components.

TABLE 8. Results of Factor Analysis[a]

factor 1 (53.7%)[b]		factor 2 (22.4%)[b]		factor 3 (11.8%)[b]	
VOC	coeff	VOC	coeff	VOC	coeff
p-xylene	0.969	pyridine	0.975	1,4-DCB	0.950
o-xylene	0.954	3-EP	0.947	1,3,5-TMB	0.807
m-xylene	0.946	1,3-butadiene	0.937	1,2,4-TMB	0.801
ethylbenzene	0.927	benzene	0.781	*p*-IPT	0.754
toluene	0.760	styrene	0.776	naphthalene	0.683
1,2,4-TMB	0.571				
1,3,5-TMB	0.556				

[a] 1,2,4-TMB (1,2,4-trimethylbenzene), 1,3,5-TMB (1,3,5-trimethylbenzene), 3-EP (3-ethenylpyridine), 1,4-DCB (1,4-dichlorobenzene), *p*-IPT (*p*-isopropyltoluene). [b] The percent of variance explained by each factor.

Several previous studies have quantified the contribution of ETS to concentrations of VOCs using an ETS source profile expressed as the ratios of 3-ethenylpyridine to target VOCs

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TABLE 9. A Comparison of Previously Reported 3-Ethenylpyridine (3-EP) to VOC Ratios in ETS with Those Recorded in This Study

	ratio (3-EP:VOC)					VOC concns ($\mu g\ m^{-3}$) in room	
VOC	(14)	(19)	(20)	(21)	this study	after smoking	before smoking
1,3-butadiene	NA[a]	NA[a]	0.77	NA[a]	0.61	24.8	0.2
benzene	1.14	1.63	1.03	0.93	0.39	42.5	4.1
toluene	NA[a]	1.00	0.58	0.58	0.20	80.7	7.5
ethylbenzene	NA[a]	6.50	3.61	3.89	2.91	6.0	0.9
p-xylene	NA[a]	NA[a]	4.59	5.96	4.33	3.4	0.7
m-xylene	NA[a]	NA[a]	1.64	1.54	1.13	13.2	2.1
o-xylene	NA[a]	9.90	4.90	7.30	6.58	2.9	0.7
1,3,5-TMB	NA[a]	NA[a]	20.64	NA[a]	61.63	0.4	0.1
styrene	3.00	4.50	3.07	3.17	3.17	5.0	0.3
pyridine	NA[a]	1.53	1.33	1.41	1.28	11.6	NA[a]

[a] NA = not available.

(*8, 9, 19*). Unsurprisingly—given inter alia the range of cigarette brands available—the ETS source profiles vary for each of the cited studies (Table 9). As a result, we generated our own ETS source profile. To do so, three cigarettes were smoked by a human volunteer for 10 min prior to sample collection inside an unventilated room. A sample was also collected prior to commencement of smoking. Concentrations of VOCs recorded both pre- and post-smoking are given in Table 9. An ETS source profile was subsequently calculated by subtracting VOC concentrations recorded prior to smoking from those detected after smoking, with the resulting 3-ethenylpyridine to VOC ratios compared with previously reported data in Table 9. As the source profile used is crucial to the estimation of the ETS contribution, we then calculated ETS contributions to VOC concentrations in each of the smoking homes studied, using the source profiles from both our own experiment and previous studies (*14, 19–21*). To illustrate, the contribution of ETS to 1,3-butadiene concentrations was calculated via the equation below

$$\text{ETS contribution (\%)} = \frac{3EP_S \times 1{,}3Butadiene_E}{3EP_E \times 1{,}3Butadiene_S} \times 100$$

where $3EP_S$ and $1{,}3Butadiene_S$ are concentrations of 3-ethenylpyridine and 1,3-butadiene in the sample and $3EP_E$ and $1{,}3Butadiene_E$ are concentrations of 3-ethenylpyridine and 1,3-butadiene in ETS.

Table 10 gives the estimated contributions of ETS to concentrations of VOCs in smoking homes monitored in this study calculated for each ETS source profile. There is appreciable variation in the estimated ETS contributions, both between homes and for the same homes using different source profiles. However, on average, ETS is shown to be the principal source of 1,3-butadiene and pyridine to the six smoking homes in this study. ETS is also indicated as a significant source of styrene in these homes and—depending on the source profile used—is a minor but appreciable source of the other monoaromatic hydrocarbons in this study. Overall, these data support the findings of our correlation and factor analysis, except that ETS was not confirmed as a significant source of benzene in our smoking homes. Clearly, the estimates of ETS contribution in Table 10 are subject to uncertainty, owing inter alia to the variability in ETS composition reported by ourselves and previous studies (*14, 19–21*). However, we believe that Table 10 provides a reasonable estimate of the relative contribution of ETS to VOC concentrations in the small number of homes we studied, while acknowledging that ETS contributions in other smoking microenvironments will vary according to factors such as cigarette brand and smoking density, etc.

The contribution of ETS to concentrations of individual VOCs has been the subject of numerous previous studies (*8, 9, 14, 19*). Interestingly, when VOC concentrations in smoking and nonsmoking indoor environments were compared in one study, although concentrations of benzene and styrene were statistically significantly higher in smoking compared to nonsmoking environments, correlation and factor analysis failed to provide evidence of a relationship between concentrations of these VOCs and those of 3-ethenylpyridine. As a result, ETS was not identified as the dominant source of benzene and styrene (*8*). In contrast, despite recording statistically significantly higher concentrations of 1,3-butadiene and benzene—but *not* styrene—in smoking homes, our more limited dataset (six smoking homes and 32 samples, compared to 25 smoking homes and 25 samples in ref *8*) demonstrates significant correlation between indoor concentrations of 1,3-butadiene, benzene, and styrene and those of the ETS marker 3-ethenylpyridine. Clearly, more research is required to clarify the significance of ETS as a source of benzene and styrene.

This study presents evidence that ETS is an appreciable source of 1,3-butadiene and styrene in the small number of smoking microenvironments studied in this project. Though the evidence for ETS being the *principal* source of styrene in the smoking homes studied is inconclusive, ETS appears to be the principal contributor to concentrations of 1,3-butadiene in such microenvironments. This conclusion is derived from the fact that concentrations of 1,3-butadiene in pubs (a smoking microenvironment) were higher than those at heavily trafficked roadside locations and in buses and trains; and that of the VOCs monitored, concentrations of 1,3-butadiene showed the highest elevation in smoking compared to nonsmoking homes. Furthermore, correlation and factor analyses both demonstrated significant correlation

TABLE 10. Summary of Estimated Contributions (%) of ETS to VOC Concentrations in Six Smoking Homes Using Different ETS Emission Profiles

	this study's ETS profile			ETS profile of (*20*)			ETS profile of (*21*)			ETS profile of (*19*)			ETS profile of (*14*)		
VOC	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1,3-butadiene	70.0	41.0	>100	60.6	32.5	99.1	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
benzene	12.3	5.3	17.7	4.7	2.0	6.7	5.2	2.2	7.4	2.9	1.3	4.2	4.2	1.8	6.0
toluene	12.5	5.2	23.5	4.3	1.8	8.1	4.3	1.8	8.1	2.5	1.0	4.7	NA[a]	NA[a]	NA[a]
ethyl benzene	13.4	5.1	24.7	10.8	4.1	19.9	10.1	3.8	18.4	6.0	2.3	11.0	NA[a]	NA[a]	NA[a]
p-xylene	11.8	4.0	23.3	11.1	3.8	22.0	8.6	2.9	16.9	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
m-xylene	15.3	5.4	30.5	10.5	3.7	21.0	11.2	4.0	22.4	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
o-xylene	8.2	2.3	17.3	11.0	3.1	23.2	7.4	2.1	15.6	5.4	1.5	11.5	NA[a]	NA[a]	NA[a]
1,3,5-TMB	5.4	0.5	10.9	16.2	1.4	32.6	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
styrene	30.8	13.9	46.1	31.8	14.4	47.6	30.8	13.9	46.1	21.7	9.8	32.4	NA[a]	NA[a]	NA[a]
pyridine	79.3	40.3	92.7	76.3	38.8	89.2	72.0	36.6	84.2	66.4	33.7	77.6	NA[a]	NA[a]	NA[a]

[a] NA = not available.

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between concentrations of 3-ethenylpyridine (an ETS marker) and 1,3-butadiene in six smoking homes. It is also shown that VOC concentrations in some microenvironments such as automobiles, pubs, and train stations can exceed those at heavily trafficked roadside locations and that in poorly ventilated homes, indoor emission sources are the most significant influence on concentrations of VOCs.

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